



Boiling point of levoglucosan and devolatilization temperatures in cellulose pyrolysis measured at different heating area temperatures

Taeko Shoji, Haruo Kawamoto*, Shiro Saka

Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

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ABSTRACT

Fast heating conditions are known to improve the yields of volatile products in cellulose pyrolysis. The mechanism, however, is not yet well understood. For better understanding of the cellulose fast pyrolysis, the devolatilization temperature was directly measured during the pyrolysis of cellulose. An *in situ* measurement method employing a very fine thermocouple was first developed. A sample in a ceramic boat was pushed into the heating area, preheated at 430–700 °C under the flow of N₂ (150 mL/min). Employing this method, the boiling point (385 °C) of levoglucosan, the major volatile product derived from cellulose fast pyrolysis, was measured directly for the first time, and was found to reduce to 345 and 292 °C under reduced pressures of 0.5 and 0.1 atm, respectively. High heating area temperatures increased the selectivity of levoglucosan evaporation by shortening the period required for the completion of evaporation. With these results in mind, pyrolysis of cellulose powder (Ceolus FD-F20) was studied using a similar procedure. The results obtained under the reduced pressures suggested that the depolymerization of cellulose, not evaporation of the volatiles products, is the rate-determining step for the pyrolytic devolatilization of cellulose. Interestingly, the depolymerization temperature varied depending on the heating area temperature as 360–385 °C (for 430–500 °C) and 400–450 °C (for 500–700 °C) (the values in the parentheses: heating area temperatures). The char morphology also changed; the pyrolysis conditions provided powder-like and film-like char materials, respectively. According to these results, the effects of heating area temperature on the cellulose pyrolysis mechanism are discussed, focusing on the behavior of cellulose crystallites.

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1. Introduction

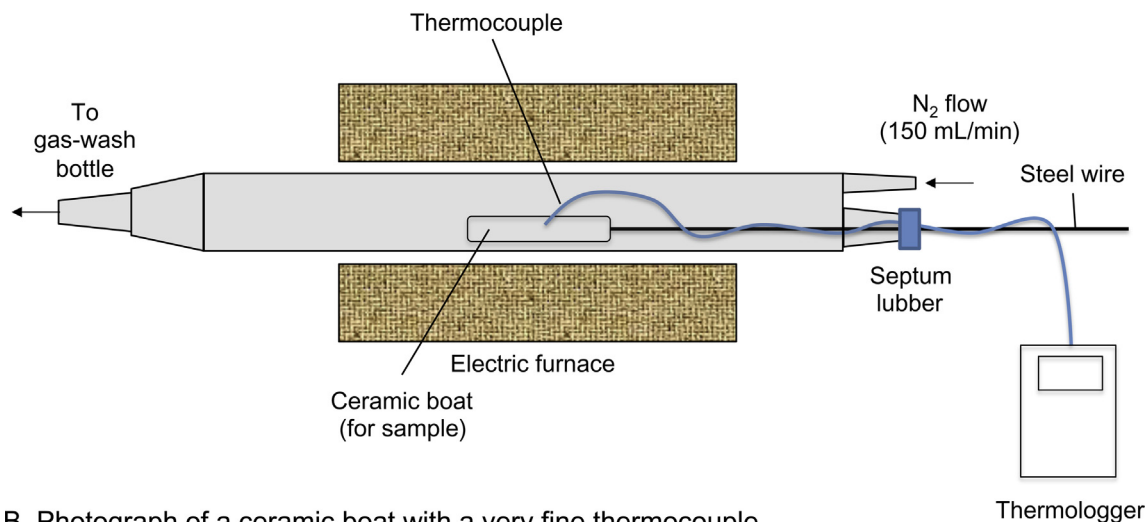
Cellulose is a major chemical constituent of wood and other lignocellulosic biomasses that are expected to be potential renewable resources for fuels, materials and chemicals. Pyrolysis, which is defined as high-temperature decomposition under the limited amount of oxygen, is a promising way to convert biomass effectively to gas, liquid and solid substances. Fast pyrolysis is a technology used to obtain liquid products—so-called “bio-oil”—and is characterized by fast heating and quick quenching of the product vapors [1–3]. During the last three decades, many studies on the fundamentals and applications of fast-pyrolysis processes have been conducted in an effort to obtain liquid fuels and useful chemicals such as levoglucosan (1,6-anhydro-β-D-glucopyranose), anhydro-oligosaccharides, glycolaldehyde, and phenols [2,4,5].

One of the most important findings in this field is the formation of liquid intermediates [6–12]. Boutin et al. [7] reported that cellulose char obtained with an image furnace had no fibrillar structure, and they explained this by the existence of liquid intermediates during pyrolysis. They also estimated the lifetime of these molten species to be lower than 1 s. In a subsequent paper reporting data of mass spectrometry and liquid chromatography/mass spectrometry analyses, Lédé et al. [8] found that the liquid intermediates mainly consisted of anhydro-oligosaccharides. Interestingly, the yields and compositions of liquid intermediates were rather constant during pyrolysis, and the mass loss and char formation started after the yield of liquid intermediates reached a steady state. From these findings, Lédé and his co-workers proposed that the formation of the liquid intermediates is the initial step in the fast pyrolysis of cellulose.

As for the anhydro-oligosaccharide formation, Suzuki et al. [13] identified cellotriosan, cellobiosan and levoglucosan from cellulose pyrolysis products obtained with CO₂ laser irradiation. Because these compounds had only 1 → 4-β-glucosidic linkages,

* Corresponding author. Tel.: +81 75 753 4737; fax: +81 75 753 4737.
E-mail address: kawamoto@energy.kyoto-u.ac.jp (H. Kawamoto).

A. Schematic diagram of reactor



B. Photograph of a ceramic boat with a very fine thermocouple



Fig. 1. Schematic diagram of the experimental set up used for the boiling point measurement and *in situ* temperature measurement during the pyrolysis of cellulose and levoglucosan.

they concluded that the anhydro-oligosaccharides are formed by cleavage of the glucosidic bonds in cellulose. Radlein et al. [14] also identified cellobiosan in 6–15% yields in syrups obtained from the fast pyrolysis of Avicel cellulose. On the basis of such high yield formation of cellobiosan, they proposed a new pathway in which the depolymerization of cellulose gives cellobiosan as a primary pyrolysis product. Their research group further identified anhydro-oligosaccharides up to heptamer from pyrolysis of cellulose at wall temperatures of 850–1200 °C and very short residence times of 35–75 ms [15]. Anhydro-oligosaccharide formation was also indicated by platinum-filament pyrolysis desorption chemical ionization mass spectrometry of cellulose [16].

Heat and mass transfer limitations relating to the fast pyrolysis of cellulose have been discussed extensively [17–20]. Secondary reactions including the repolymerization of levoglucosan [21–23] as the major primary product from cellulose as well as other gas- and liquid-phase reactions reduce the bio-oil yields by increasing the char and/or gas yield. Thus, mass-transfer efficiencies of liquid- and vapor-phase products are normally important in the high-yield formation of volatile products; i.e., bio-oil.

One of the major problems encountered during the investigation of cellulose fast pyrolysis is the uncertainty of the actual pyrolysis temperature [17,19,20]. Heat-transfer limitations from the reactor to sample, lags in the recordings of the measuring devices and endothermic processes have been considered as the origin of this problem. From theoretical calculation results, L     and Villiermaux [20] and Narayan and Antal [19] indicated that the true sample temperature remains almost constant during pyrolysis even if the reactor temperature is much higher. This was confirmed by Lanzetta et al. [17], who measured the surface temperature of a thin powdered cellulose layer by direct physical contact with a thin (0.1-mm bead) thermocouple during fast pyrolysis with a radiant heater in the temperature range 250–426 °C. They confirmed that a region existed where the sample temperatures were significantly

lower than the temperature obtained when char was heated in a control experiment. Similar direct temperature measurements have been conducted to obtain the temperature profiles of the surface and interior of wood specimens during pyrolysis [24–30]. In spite of these extensive studies, actual pyrolysis temperature of cellulose has not yet been fully clarified.

This article deals with the devolatilization temperatures of cellulose, along with the boiling point of levoglucosan as the major volatile product. A direct temperature measurement method by contacting a very fine thermocouple to sample was developed first and evaluated by the measurement of the boiling points of some thermally stable aromatic compounds. With this method, the boiling point of levoglucosan was measured for the first time. Temperature of cellulose during pyrolysis was then measured with the same method when cellulose was inserted into the heating area at different temperatures between 430 and 700 °C. Since the devolatilization process lowered the heating up efficiency of cellulose due to its large endothermicity, the resulting temperature profile gave us some insight into the temperatures of cellulose depolymerization and the following volatilization. The heating area temperature may affect the heating up process of cellulose under the influence of these endothermic processes. Finally, according to these experimental results, the paper discusses mechanisms of the volatiles formation during cellulose pyrolysis, focusing on the response of cellulose crystallites at different heating area temperatures.

2. Materials and methods

2.1. Materials

1,3,5-Triphenylbenzene (>99.0%), 1,2-benzanthraquinone (>95.0%), levoglucosan (>99.0%) (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), anthraquinone (>98.0%) (Nacalai Tesque,

Inc., Kyoto, Japan) and 9-phenylacridine (96+%) (Wako Pure Chemical Industries, Ltd., Osaka, Japan) were used without further purification. Microcrystalline cellulose powder (Ceolus FD-F20, Asahi Kasei Chemicals Corporation, Tokyo, Japan) was used as a cellulose sample. Other solvents and chemicals were purchased from Nacalai Tesque, Inc., Kyoto, Japan.

2.2. Direct temperature measurement during heat-treatment

A schematic diagram of the reactor used in this study is shown in Fig. 1A. Sample (40 mg) was taken in a ceramic boat [6 mm (W) × 30 mm (L) × 4 mm (D), Nikkato Corporation, Osaka, Japan], and tip of a fine thermocouple (0.25 mm in diameter, type K, Shinnetsu Co., Ltd., Ibaraki, Japan) connected to a thermologger (AM-8000, Anritsu Corporation, Kanagawa, Japan) was placed in the sample layer without contacting the bottom of the ceramic boat (Fig. 1(B)). A steel wire was attached to one end of the ceramic boat, and the ceramic boat was placed at the right end of a quartz glass tube (internal diameter 12 mm, length 400 mm, wall thickness 1 mm) through a tiny hole of a septum rubber. Thus, the ceramic boat could be pushed into the heating area, maintaining the sealing between the wire and the septum rubber. About half of the tube was heated to a desired temperature between 350 and 700 °C in a cylindrical electrical heater under a nitrogen flow (150 mL/min), and then the ceramic boat was inserted immediately to the center of the heating area. After 10 min, the ceramic boat was pulled out from the heating area. The heating area temperature was monitored in a blank test by inserting the thermocouple into the center of the heating area, and the furnace temperature was set to maintain the heating area at the desired temperature. The gas residence time was around 10 s with this system. To confirm the reproducibility of the temperature profile obtained with this *in situ* measurement method, we repeated the measurement at least three times to get the similar temperature profiles. When the thermocouple did not contact to the sample properly, precise temperature profile could not be obtained.

The volatile materials generated from the heat-treatment of levoglucosan and cellulose were collected with a gas-washing bottle containing a mixture of MeOH/CHCl₃ (1/5, v/v, 10 mL) which was connected to the left end of the quartz glass tube through a Teflon tube. No additional cooling device was used. The condensates observed on the tube wall were rinsed with the MeOH/CHCl₃ solution repeatedly. The solutions were combined and evaporated in vacuo. The resulting materials were solubilized in D₂O (1.0 mL) and analyzed with ¹H NMR on a Bruker AC-400 (400 MHz) spectrometer. Chemical shifts (δ) are given in ppm.

The residues (char) attaching to the bottom of the ceramic boat after heat-treatment of levoglucosan were rinsed with water (5 mL) and dried in an oven (105 °C) for 24 h. The amount of water-insoluble char was obtained by subtracting the weight of ceramic boat after incineration at 600 °C for 2 h from the weight.

The experiments under the reduced pressures were conducted by modifying the above-mentioned procedure. A vacuum pump and a vacuum controller (VCN-500, Okano Works, Ltd., Osaka, Japan) were connected to the gas-washing bottle through a Teflon tube to reduce the pressure inside the quartz glass tube. The pressure of the pyrolysis system was monitored with the vacuum controller. The ceramic boat with sample and the thermocouple was placed in the left end of the tube and pulled into the heating zone after the temperature and the pressure reached the desired values. After the exchange of the air inside the reactor with nitrogen, the nitrogen flow stopped during the heat-treatment experiment.

2.3. Chemical analyses of pyrolysis products from levoglucosan

Pyrolysis of levoglucosan was conducted at the heating area temperature 350 °C with the procedure described above. The heating time of the ceramic boat with sample was changed from 1 to 10 min, and the pyrolysis products in the ceramic boat were separated into the water-soluble portions and insoluble char by the extraction of the residues remaining in the ceramic boat with water (5.0 mL). The amounts of water-soluble portion and char were determined from the weight difference before and after the extraction and the following incineration at 600 °C for 2 h.

One mL of the water-soluble portion was taken in a vial, and tri-fluoroacetic acid (0.18 mL) was added to the solution. The resulting solution was heated in an autoclave (120 °C) for 60 min to hydrolyze anhydro- and oligo-/poly-saccharides into monosugars. The reaction mixture was evaporated in vacuo, redissolved in D₂O (1.0 mL) containing 2-furancarboxylic acid as an internal standard and analyzed by ¹H NMR. Sugar yields were determined from the relative peak areas of the C1-protons against the signals of the internal standard.

The water-soluble portions were also analyzed by gel permeation chromatography (GPC) with a Shimadzu LC-10A under the chromatographic conditions of column: Asahipac GS-220HQ, eluent: water, column temperature: 60 °C, flow rate: 0.5 mL/min, detector: RI.

3. Results and discussion

3.1. A direct boiling-point measurement method verified for thermally stable aromatic compounds

Information on the boiling points of volatile products from cellulose pyrolysis is important to the understanding and control of pyrolysis processes, since secondary decomposition pathways of these volatile products are suggested to be different for liquid and gas phases. Hosoya et al. [31] reported that the pyrolytic pathway of levoglucosan as an important primary product derived from cellulose was completely different for the gas and liquid phases. Thus, the boiling point of levoglucosan is especially important. However, no direct measurement has been made for levoglucosan owing to polymerization occurring above 240 °C [32,33], which is much lower than the estimated boiling point [18,34] of levoglucosan and the temperature of formation (>300 °C) from cellulose [35,36]. Accordingly, one of the objectives of this paper is the measurement of the boiling point of levoglucosan.

The melting of a crystalline substance and the boiling of a liquid substance are both endothermic processes, and hence, these temperatures can be measured by thermal analysis techniques including differential scanning calorimetry. However, such a method is usually conducted under slow heating conditions and cannot be conducted under fast-pyrolysis conditions. We considered that the method of measuring temperature through direct physical contact with a fine thermocouple is suitable for this purpose. Accordingly, the applicability of the method to the measurement of melting (mp) and boiling (bp) points was first verified using thermally stable aromatic compounds.

Fig. 2 shows the temperature profiles obtained for 1,3,5-triphenylbenzene (mp: 176 °C, bp: 462 °C), anthraquinone (mp: 286 °C, bp: 377 °C), 9-phenylacridine (mp: 404 °C, bp: 184 °C) and 1,2-benzanthraquinone (mp: 166–171 °C, bp: 472 ± 15 °C) with the apparatus shown in Fig. 1. The boiling point of the last compound is an estimated value [34], since no measurement has been made, probably owing to the instability. Other melting points and boiling points are the experimental data obtained from the data source, the PhysProp Database (Syracuse Research Corp., Syracuse, NY). In all

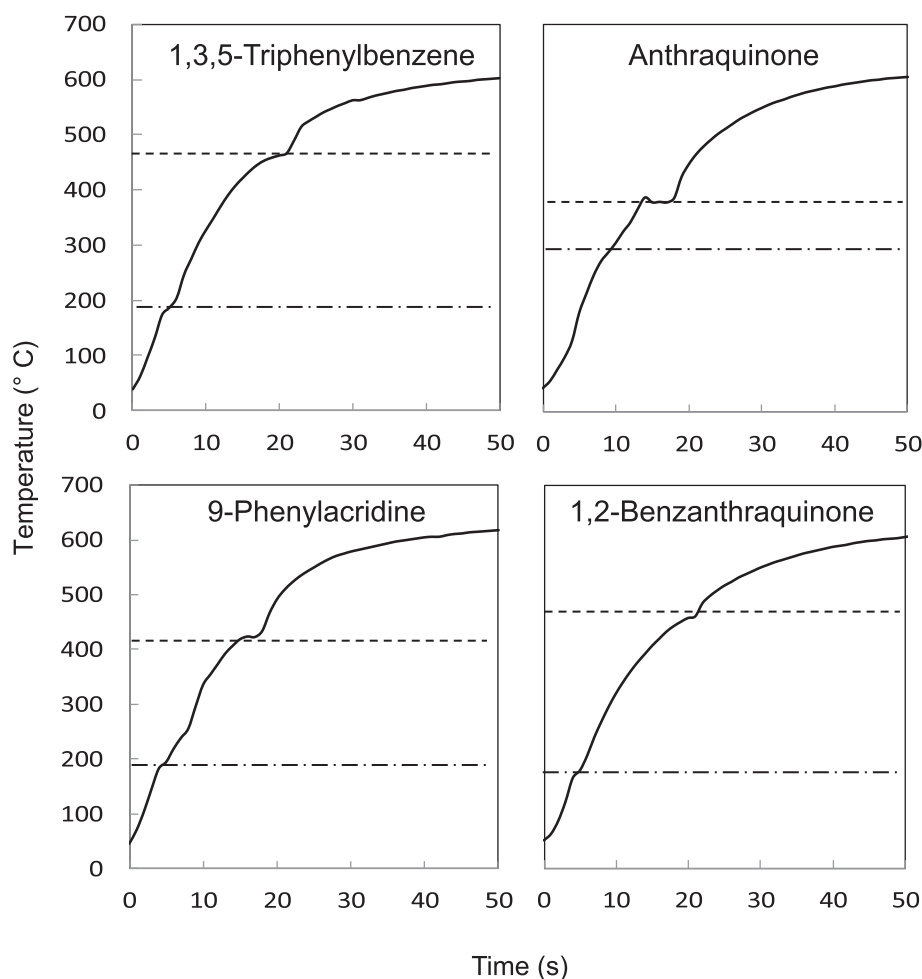


Fig. 2. Temperature profiles obtained for heating various aromatic substances (heating area temperature: 600 °C). — · — · —: melting point reported, — · — · —: boiling point reported or estimated.

temperature profiles, clear plateaus are observed in the temperature ranges corresponding to the reported and estimated melting and boiling points even for such fast heating conditions. A long response time of the thermocouple may reduce the accuracy of the *in situ* temperature measurement, whereas it took only about 3 s for the measured temperature to reach the heating area temperature, when only the thermocouple was inserted into the heating area (600 °C) in a blank test. Thus, boiling points can be measured fairly precisely along with the melting point using the present *in situ* temperature measurement method. These results also suggest that the temperature measurement of sample in the ceramic boat is quite accurate with this method.

3.2. *In situ* temperature measurement during pyrolysis of levoglucosan and cellulose

Employing the *in situ* temperature measurement method, temperature profiles were obtained during the pyrolysis of levoglucosan and cellulose at heating area temperatures of 430–700 °C under a flow of nitrogen (150 mL/min). The profiles obtained under atmospheric and reduced pressures are illustrated in Figs. 3 and 4, respectively. Under reduced-pressure conditions, no nitrogen flow was applied. Fig. 5 shows ¹H NMR spectra of the volatile products, obtained from levoglucosan and cellulose at a heating area temperature of 600 °C, compared with that of pure levoglucosan.

3.2.1. Levoglucosan and its boiling point

Temperature discontinuities, due to endothermic processes, are observed at approximately 320–385 °C along with smaller ones around 120–140 °C and 230–240 °C (Fig. 3). The latter two observations can be interpreted with thermogravimetric analysis data on levoglucosan reported by Shafizadeh and co-workers [37–39]; they observed several endothermic signals around 110–115 °C and identified as the transitions between several crystalline forms [38]. They also found an endothermic signal at 137 °C, which was assigned to the plastic crystal transition [38]. Accordingly, the temperature discontinuities observed at 120–140 °C in Fig. 3 would originate from these crystalline transformations before the pyrolytic reactions occur.

Levoglucosan polymerizes at approximately 240 °C even in its pure form. Shafizadeh et al. [39] noted the broad endothermic signal in the temperature range 200–300 °C in thermogravimetric analysis, which corresponds to the polymerization. The temperature discontinuities around 230–240 °C observed in the profiles (for heating area temperatures of 430 and 600 °C) (Fig. 3) reflect the polymerization reactions of levoglucosan.

The plateaus (approximately 320–385 °C) are suggested to arise from the evaporation of levoglucosan. With an increase in the heating area temperature, this plateau moves to higher temperatures and becomes constant at 385 °C (heating area temperatures of 550, 600 and 650 °C, Fig. 3). This temperature (385 °C) reduced to 345 and 292 °C when the experiments were conducted under

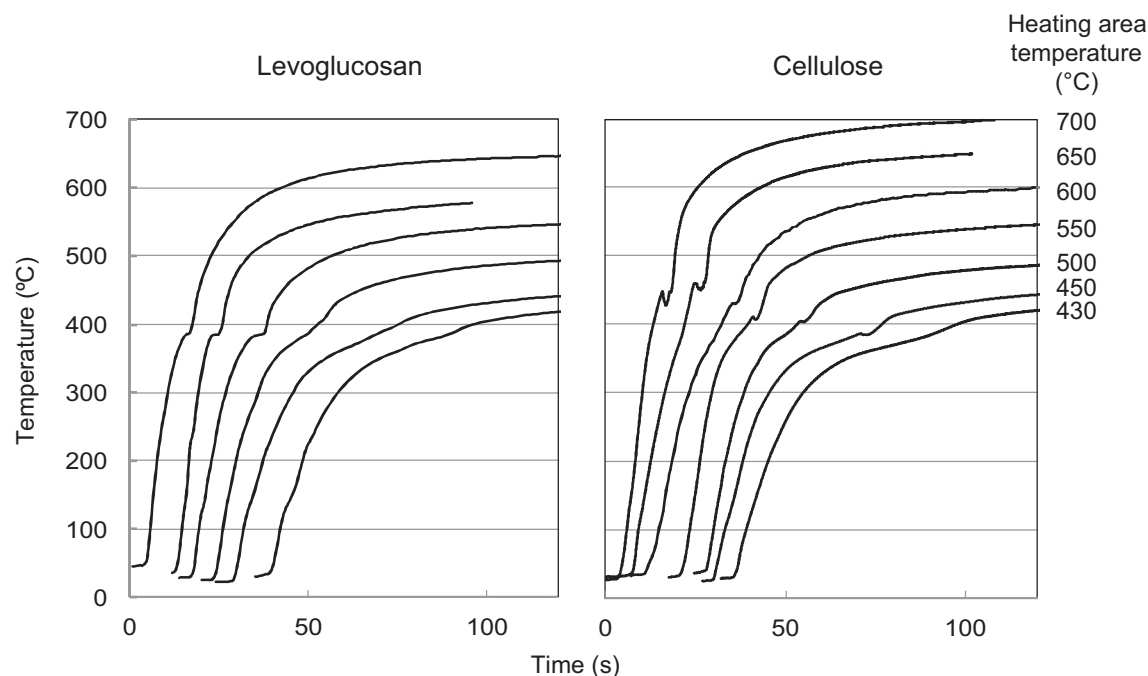


Fig. 3. Temperature profiles obtained during the heat treatment of levoglucosan and cellulose under atmospheric pressure (heating area temperature: 430–700 °C).

reduced pressures of 0.5 and 0.1 atm, respectively, for both heating area temperatures of 600 and 430 °C (Fig. 4). Furthermore, the ^1H NMR spectrum in Fig. 5 indicates that levoglucosan was exclusively observed as a volatile product from levoglucosan pyrolysis, although some very small signals mainly assigned to the protons of 1,6-anhydro- β -D-glucofuranose (AF, with solid circle markers) are also included. These observations clearly indicate that the plateaus at 385 °C (heating area temperatures of 550, 600 and 650 °C) originate from the evaporation of a single compound; i.e., levoglucosan. Accordingly, the boiling point of levoglucosan (385 °C) under normal pressure was directly measured for the first time. Later discussion on the transformation of levoglucosan at a heating area temperature of 350 °C supports this conclusion.

At the lowest heating area temperature of 430 °C, the evaporation of levoglucosan started at temperatures lower than the boiling point of levoglucosan, and the plateau (385 °C) is hence ambiguous in Fig. 3. Under reduced pressure, the boiling-point plateau became much clearer (Fig. 4). This could be explained by the lower boiling points of levoglucosan under reduced pressures. The appearance of a clear boiling-point plateau may require a minimum difference between the heating area temperature and boiling point.

3.2.2. Cellulose

Fig. 5 indicates that levoglucosan is the major volatile product derived from cellulose pyrolysis under the present conditions. The formation of AF was also observed in a higher yield than the pyrolysis of levoglucosan; levoglucosan/AF molar ratio: 1.0/0.12 for

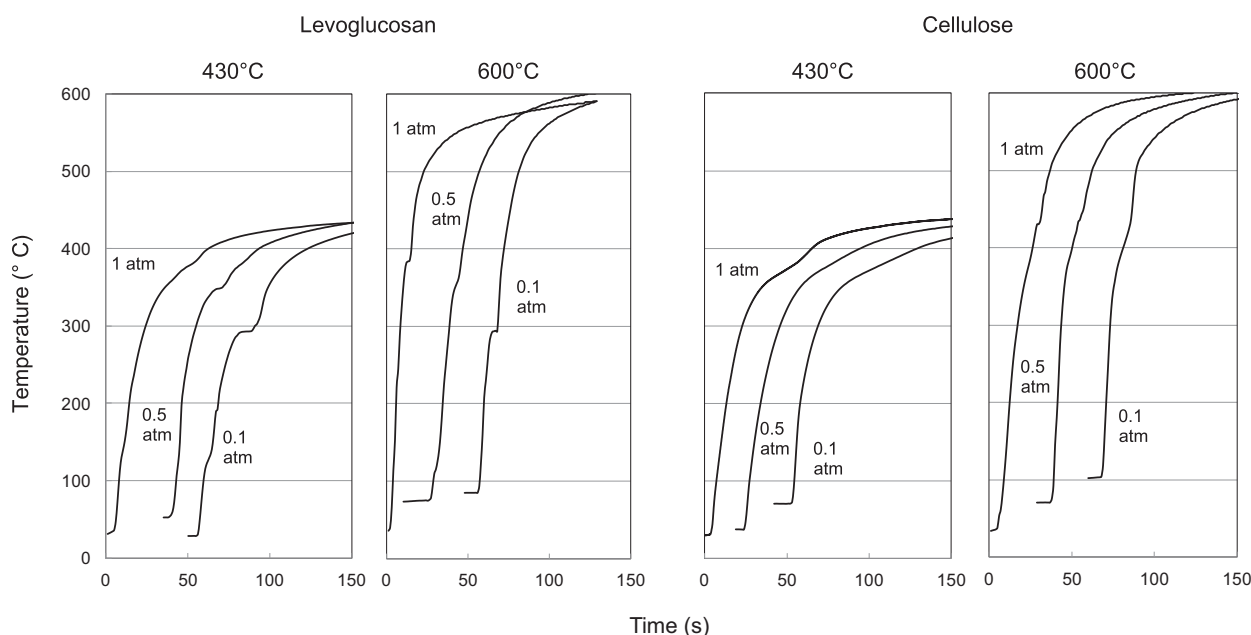


Fig. 4. Temperature profiles obtained during the heat treatment of levoglucosan and cellulose under reduced pressures (heating area temperature: 430 and 650 °C).

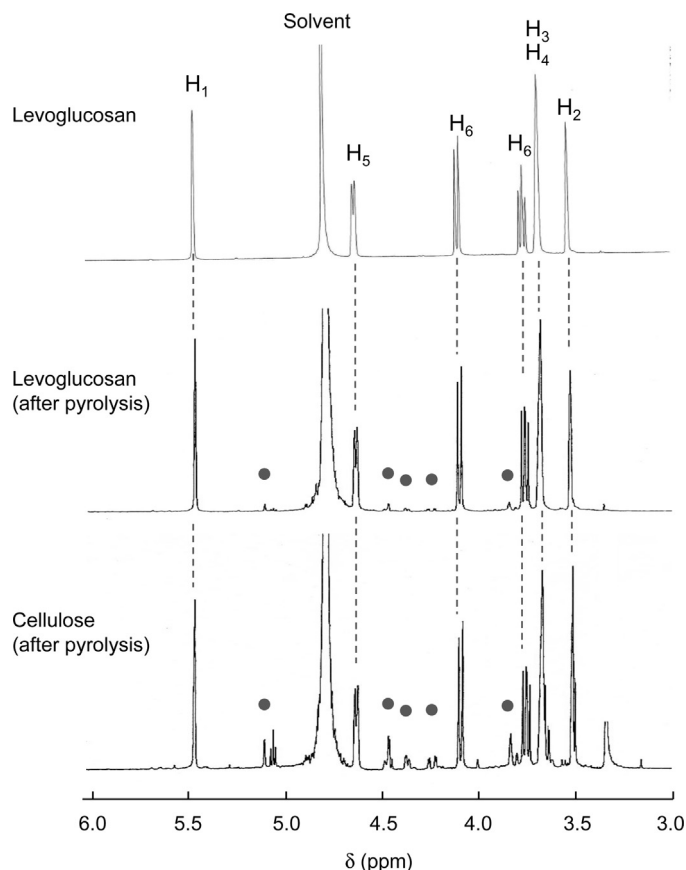


Fig. 5. ^1H NMR spectra of the volatile materials obtained from the pyrolysis of levoglucosan and cellulose (heating area temperature: 600°C). ●: signals assigned to 1,6-anhydro- β -D-glucofuranose (AF).

cellulose pyrolysis and 1.0/0.019 for levoglucosan pyrolysis. Thermal decomposition from the reducing ends may increase the AF yield from cellulose. Glucose, as a model of cellulose reducing end, is known to give a significant amount of AF along with levoglucosan [40,41].

The temperature profiles obtained for the cellulose pyrolysis (Fig. 3) and the influences of the vacuum conditions (Fig. 4) were quite different from those of the levoglucosan pyrolysis. The temperature profile of cellulose at the low heating area temperature 430°C , which has an endothermic devolatilization plateau around 360 – 385°C , is very similar to that of levoglucosan (430°C). This temperature range, however, did not reduce even under vacuum pyrolysis conditions (Fig. 4). Thus, the formation of volatile products (i.e., the depolymerization of cellulose) and not the evaporation of volatile products (mainly levoglucosan) is the rate-determining step for the devolatilization of cellulose.

Unlike the case of levoglucosan pyrolysis, the heating area temperature greatly affected the devolatilization temperature of cellulose, which increased to 400 – 450°C , when the heating area temperature increased to 500 – 700°C (Fig. 3). Even a temperature decrease due to the strong endothermicity of volatilization is observed clearly at heating area temperatures of 650 and 700°C . These observations indicate that the devolatilization temperatures (400 – 450°C) are higher than the boiling points of the volatile products. The devolatilization temperature ($\sim 420^\circ\text{C}$) at 600°C was also independent of the pressure of the pyrolysis environment (Fig. 4). Furthermore, the period required for the completion of devolatilization of cellulose became notably shorter at these higher heating area temperatures. All these results suggest that, at heating area temperatures of 500 – 700°C , the depolymerization of cellulose

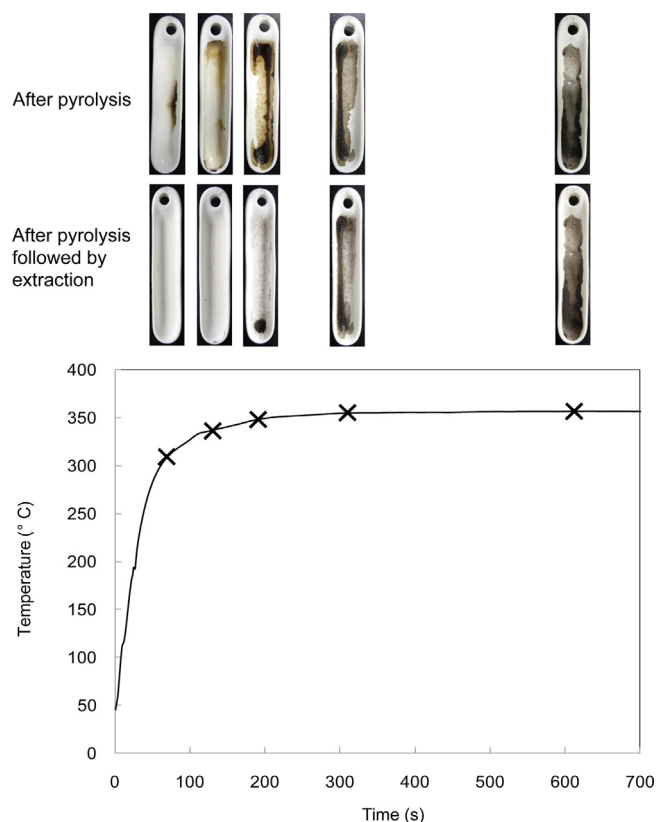


Fig. 6. Temperature profile obtained during the pyrolysis of levoglucosan (heating area temperature: 350°C) along with photographs of the ceramic boats after pyrolysis and subsequent extraction with water.

occurs quickly when the cellulose temperature reaches 400 – 450°C . This temperature range (400 – 450°C) is close to the temperature (443°C) that Boutin et al. [6] estimated for the surface between cellulose and liquid intermediates during the fast pyrolysis of cellulose on the basis of modeling results. It should be emphasized that these temperatures are higher than the boiling point (385°C) of levoglucosan as the major volatile product from cellulose. Accordingly, recovery of the volatile products through evaporation is effective under these conditions. This would be a reason why fast-pyrolysis conditions are effective for the formation of volatile products.

3.3. Behavior of levoglucosan at a furnace temperature of 350°C

For better understanding of the behavior of levoglucosan under the present experimental conditions, the products derived from levoglucosan at a heating area temperature of 350°C were characterized according to hydrolysable sugar yields and GPC analysis data. The temperature of 350°C was just below the boiling point of levoglucosan.

Fig. 6 shows the temperature profile of levoglucosan along with photographs of ceramic boats after pyrolysis and subsequent extraction with water. Transformation to dark substances was observed after 1 min of pyrolysis, while most of the substances that had formed after 1 and 2 min were soluble in water. After longer periods of pyrolysis, water-insoluble char materials formed.

The amounts of water-soluble (WS) portions obtained from levoglucosan (40 mg) are shown in Fig. 7 against the heating time and compared with the amounts of hydrolysable sugar obtained by hydrolysis of the WS portions with trifluoroacetic acid at 120°C . The resulting sugar was exclusively glucose. The amount of hydrolysable sugar given has been adjusted to the amount of anhydro-sugar by multiplying the sugar yield by $162/180$, in which

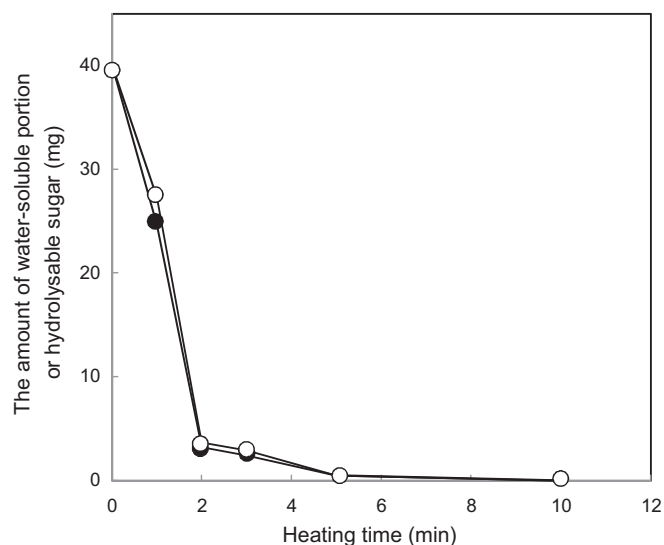


Fig. 7. Time course of the change in the amounts of the water-soluble (WS) portion and hydrolysable sugar during the pyrolysis of levoglucosan (40 mg) (heating area temperature: 350 °C). ○: water-soluble portion, ●: hydrolysable sugar. The amount of hydrolysable sugar is adjusted to the amount of anhydro-sugar by multiplied by 162/180, which are the molecular masses of anhydro-glucose and glucose, respectively.

162 and 180 are the molecular masses of anhydro-glucose and glucose, respectively. Even though the colored substances mentioned above were included in the WS portions (after 1 and 2 min), the amounts of hydrolysable sugar were very close to those of WS portions. This tendency was also observed for the products (after 3 and 5 min). These results suggest that the WS portions mainly consisted of sugar-related compounds.

GPC analysis data are presented in Fig. 8 along with a chromatogram for pure levoglucosan. Significant amounts of polymerization products are observed in the WS portions (after 2, 3 and 10 min), whereas the contents are not high in other samples. In the WS portion (after 1 min), the main peak corresponds to levoglucosan and a very small signal corresponds to dimers. As the heating time extended from 1 to 2 min, the yield of the WS portion decreased from 68 to 9 wt% and the composition changed from levoglucosan to mainly dimers. For both heating durations, no insoluble char was observed (Fig. 6). These results suggest that about 30% of levoglucosan was directly evaporated in the period to 1 min, and the evaporation competed in the period 1–2 min with the condensation reaction to dimers, which resulted in the evaporation of about 90% of levoglucosan. Polymerization of levoglucosan is suggested to be a reversible reaction [21], and hence, levoglucosan could form from the dimers and higher oligomers. However, relatively slow reduction rates of the yields of WS portions and hydrolysable sugars in the period 2–3 min indicate that the contribution of the levoglucosan evaporation via dimers/oligomers was not significant. From these considerations, it is suggested that a large portion of levoglucosan evaporated directly even at a heating area temperature of 350 °C, which is lower than the boiling point of levoglucosan. These results also support the conclusion that the plateau observed at 385 °C (Fig. 3) reflects the boiling behavior of levoglucosan.

The WS portion (after 5 min) consisted of fairly pure levoglucosan, although the yield of the WS portion was only 1.4 wt% (0.5 mg) (Fig. 8). This is an unexpected result because the polymerization products were clearly observed in the WS portion obtained after the shorter heating time of 3 min. We have reported that levoglucosan was stabilized up to 350 °C in some aromatic

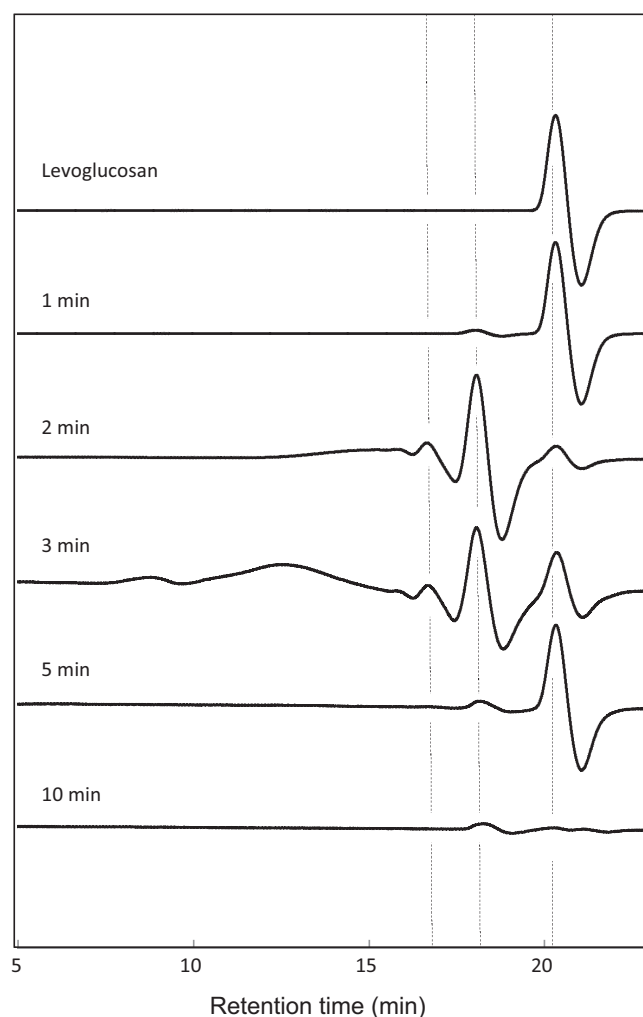


Fig. 8. GPC analyses data obtained for the water-soluble portions from levoglucosan pyrolysis with different heating times (heating area temperature: 350 °C). Column: Asahipac GS-220HQ, eluent: water, column temperature: 60 °C, flow rate: 0.5 mL/min, detector: RID.

substances [33], and proposed a stabilization mechanism [42], in which the proton donation to levoglucosan acting as the acid catalyst is inhibited by the specific hydrogen bonding between levoglucosan OH and aromatic π -electrons. Levoglucosan in the pyrolysis mixture (after 5 min) may be stabilized in char materials having an aromatic character.

The polymerization reactivity of levoglucosan seems to be lower than expected from the results of lower-temperature pyrolysis. In the proposed mechanism, as mentioned above, proton donation through intermolecular hydrogen bonding between levoglucosan molecules promotes acid-catalyzed pyrolytic reactions including transglycosylation (polymerization) and dehydration to char [42–44]. Such intermolecular hydrogen bonding may become less effective at the high temperatures used in this study.

3.4. Char formation

Char yields and photographs of ceramic boats after *in situ* temperature measurements conducted for levoglucosan and cellulose (Fig. 3, pyrolysis time of the sample in the ceramic boat: 10 min) are shown in Figs. 9 and 10, respectively. The water-insoluble char yields obtained after extraction with water are also included in Fig. 9.

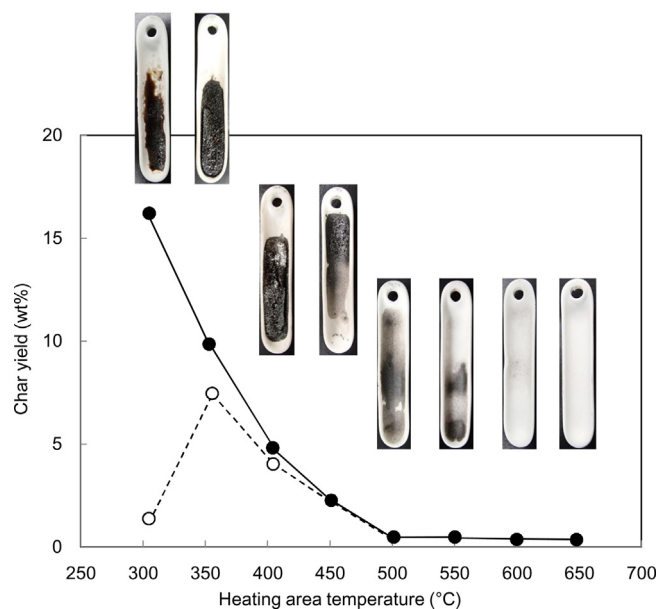


Fig. 9. Char yields from levoglucosan at different heating area temperatures (pyrolysis time: 10 min) along with photographs of ceramic boats after pyrolysis. —●—: char yield, ---○---: char yield after extraction with water.

The char yield from levoglucosan decreased with an increase in the heating area temperature and became almost zero at the temperatures above 600 °C. Conversion to water-insoluble char materials proceeded in the temperature range 300–350 °C. As discussed in Fig. 3, the period required for the completion of levoglucosan evaporation became shorter with increasing heating area temperature. Quick removal from the heating area would improve the selectivity of the levoglucosan evaporation against char formation. Thus, levoglucosan evaporated completely when sufficient heat was supplied by the heating area with higher temperatures exceeding 600 °C under the present conditions.

On the other hand, the formation of cellulose char was not inhibited completely even at a heating area temperature of 650 °C, although the char yield tended to decrease as the heating area temperature increased, except at 400 °C (Fig. 10). Even after 10 min pyrolysis, carbonization of cellulose was not effective at 300 °C. Like the case of levoglucosan pyrolysis, the carbonization

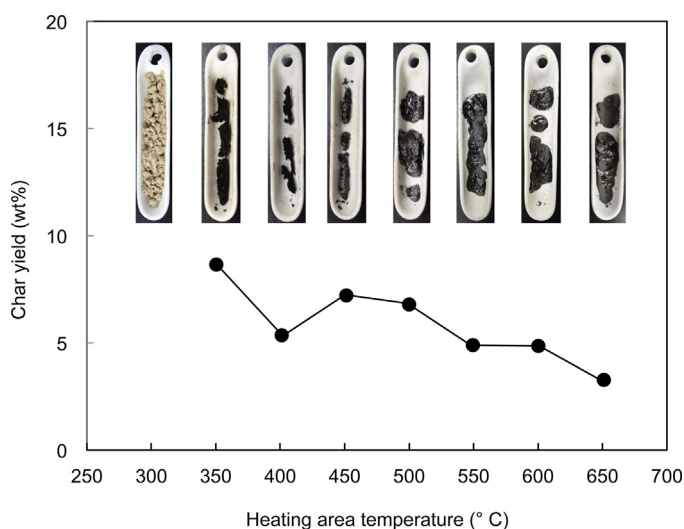


Fig. 10. Char yields from cellulose at different heating area temperatures (pyrolysis time: 10 min) along with photographs of ceramic boats after pyrolysis.

Heating
area
temperature

400°C

450°C

650°C

Fig. 11. Morphologies of char materials obtained for different heating area temperatures of 400, 450 and 650 °C (enlargements of Fig. 10).

reactivity of cellulose significantly increased in the temperature range 300–350 °C. Thus, levoglucosan is potentially converted to char in competition with evaporation and polymerization when it forms from cellulose pyrolysis. The mass-transfer efficiency also affects the char formation. The formation of volatile products (mainly levoglucosan) at cellulose temperatures exceeding 400 °C (Fig. 3) would increase the evaporation selectivity, since these temperatures are higher than the boiling point (385 °C) of levoglucosan.

The morphology of cellulose char materials changed in the temperature range 400–500 °C from powder-like (350–450 °C) to film-like (>500 °C) materials (Fig. 11). Interestingly, this transition temperature range is close to the range in which the devolatilization of cellulose shifted to a high-temperature mode (Fig. 3). Since the film-like char formation indicates the involvement of liquid intermediates, liquid intermediates are suggested to form more selectively for the high-temperature mode of cellulose depolymerization (>400 °C).

3.5. Mechanisms of cellulose pyrolysis

As summarized in Fig. 12, depolymerization of cellulose to levoglucosan occurs in different temperature ranges (i.e., 360–385 °C and 400–450 °C) depending on the heating area temperature. These results are explainable with the relationships between heat of evaporation and heat supply from the heating area. Generally, the evaporation of volatile products eliminates heat from the sample, and this lowers the sample temperature as indicated by Narayan and Antal [19].

The rate of volatiles formation would be an important factor to determine the heat demand for evaporation of the volatile products. If the heat demand which is positively related to the formation rate of the volatiles is lower than the heat supply from the heating area, the sample temperature can reach temperatures higher than the boiling points of the volatile products.

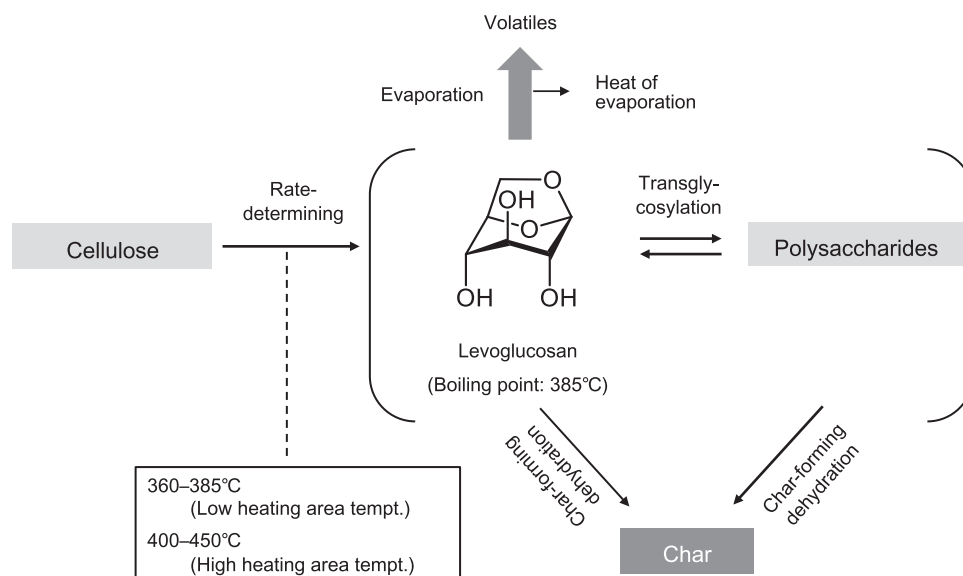


Fig. 12. Formation of levoglucosan from cellulose at different heating area temperatures and the subsequent evaporation and conversion to polysaccharides and char.

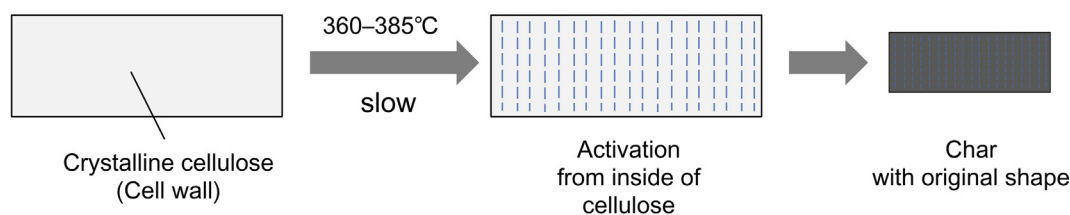
Recently, heterogeneous cellulose pyrolysis mechanisms including nucleation kinetic models have been suggested by Reynolds and Burnham [45], Capart et al. [46] and Mamleev et al. [47]. Matsuoka et al. [48] proposed an activation mechanism of cellulose occurring heterogeneously within crystalline cellulose (cell wall) (Fig. 13A); cellulose reducing ends decompose first, and this activates cellulose for pyrolytic decomposition. With this activation mechanism, cellulose decomposes heterogeneously from some end surfaces of cellulose crystallites (shown as the dotted lines in Fig. 13A), which are formed all over the cell wall,

during the initial depolymerization stage of cellulose to give the fragments with degree of polymerization of around 200. Owing to such heterogeneous decomposition, it takes a relatively long period for the pyrolysis reactions to complete, and this results in the relatively slow release of the volatile products.

In the low temperature mode, the depolymerization temperature (360–385 °C) is rather close to the boiling point of levoglucosan (385 °C) under the normal pressure. In this mode, the heat demand for evaporation may be balanced with the heat supply from the heating area at relatively low heating area temperatures <450 °C,

A. Low temperature mode (Heating area temperature: < 450°C)

Heat demand for evaporation = Heat supply from the heating area



B. High temperature mode (Heating area temperature: > 500°C)

Heat demand for evaporation < Heat supply from the heating area

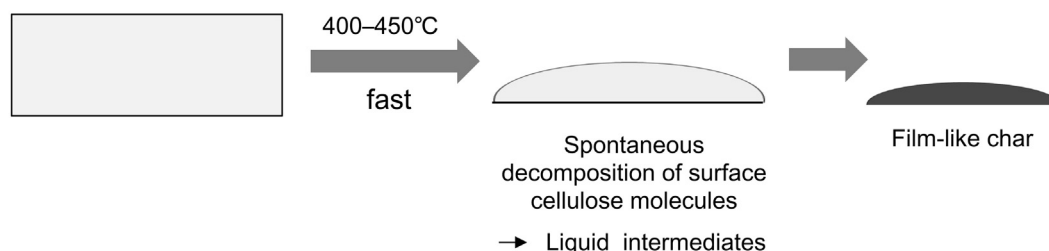


Fig. 13. Proposed molecular mechanisms in cellulose pyrolysis at different heating area temperatures, which include low- and high-temperature cellulose depolymerization modes.

and hence the sample temperature would maintain in the range of 360–385 °C before completing the devolatilization. Formation of the depolymerization products including levoglucosan and their subsequent secondary decompositions competing with evaporation (Fig. 12), which successively occur inside the crystalline cellulose (cell wall), may convert cellulose to char materials slowly while keeping its original shape by shrinking in size (Fig. 13A).

The situation changes when the heat supply from the heating area is greater than the heat demand for evaporation as shown in Fig. 13B. Under these conditions with heating area temperatures exceeding 500 °C, the cellulose temperature reached 400–450 °C, which was higher than the boiling point (385 °C) of levoglucosan as the major volatile product. At such high temperatures, the depolymerization of cellulose occurs quickly to give low-molecular-weight liquid intermediates before conversion to char materials. Surface molecules in cellulose crystallites are thought to decompose spontaneously at 400–450 °C without the activation process mentioned above, although further study is necessary to confirm this hypothesis. A charring reaction (Fig. 12) occurs after the formation of liquid intermediates, which results in the formation of film-like char. A slight increase in the char yield observed when the heating area temperature increased from 400 to 450 °C (Fig. 10) may be related to the liquefaction before char formation; in the thick liquid layer, the mass-transfer efficiency would be lower.

These results also suggest the important conclusion; the heating rate is not critical for the fast pyrolysis of cellulose, but the actual cellulose temperature is very important. Cellulose decomposition via the high temperature mode at 400–450 °C (Fig. 13B) gives liquid intermediates quickly, and the following efficient evaporation would enhance the formation of volatile products from cellulose. These conditions can be accomplished by the excessive supply of heat to the cellulose during the relatively slow devolatilization occurring via the low temperature mode (Fig. 13A).

4. Conclusions

1. An *in situ* measurement method was exploited to obtain boiling and melting points.
2. The boiling point of levoglucosan was directly measured to be 385 °C, which decreased to 345 and 292 °C under reduced pressures of 0.5 and 0.1 atm, respectively.
3. The evaporation of levoglucosan was complete in a shorter period at a higher heating area temperature, which increased the selectivity of the evaporation against condensation and charring reactions.
4. The depolymerization of cellulose and not the evaporation of volatile products was the rate-determining step for the devolatilization of cellulose.
5. The temperature of cellulose depolymerization depended on the heating area temperature; 360–385 °C for low heating area temperatures of 430 and 450 °C and 400–450 °C for high heating area temperatures of 500–700 °C.
6. The cellulose char morphology also depended on the heating area temperature. The morphology was powder-like at low heating area temperatures of 430 and 450 °C and was film-like at high heating area temperatures of 500–700 °C.
7. A molecular mechanism of cellulose pyrolysis was proposed, which includes low and high temperature devolatilization modes. In the low-temperature mode, cellulose is pyrolyzed slowly and heterogeneously with activation within cellulose, whereas in the high-temperature mode, spontaneous depolymerization of cellulose surface molecules occurs quickly without via the activation process.
8. It was concluded that the heating rate is not critical for the fast pyrolysis of cellulose, but the actual cellulose temperature is

rather important; the high temperature mode of devolatilization enhances the formation of volatile products from cellulose through quick liquefaction and the following efficient evaporation.

9. Heat demand for evaporation and heat supply from the heating area were proposed as a key factor for determining the high and low temperature devolatilization modes for cellulose pyrolysis.

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